Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Vanadium(V) in Perchloric Acid Medium

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The oxidation kinetics of benzaldehyde and its substituted derivatives by vanadium(V) have been studied in perchloric acid medium. The reaction is first order in both [vanadium(V)] and [H$^+$] whereas the order with respect to [substrate] is less than unity. The kinetic and spectrophotometric results indicate the formation of an intermediate 1 : 1 complex between the reactive vanadium(V) species and hydrated benzaldehyde prior to electron transfer. Thermodynamic parameters associated with the intermediate complex and activation parameters for the slow step have been evaluated. The reaction is found to have a significant deuterium isotope effect. A mechanism consistent with the experimental observations is proposed.

The stoicheiometry, kinetics, and mechanism of the reduction of vanadium(V) by a multitude of organic species[1-9] have been studied. Littler and Waters[4] have shown that most, if not all, such reactions proceed *via* a free radical mechanism. The alternative sequence where vanadium(V) undergoes two-electron reduction followed by rapid vanadium(V) oxidation of a vanadium(III) intermediate to vanadium(IV) has also been suggested.[10-12] The metal ion oxidations of benzaldehyde in acidic and alkaline media have been reported.[13-18] Benzaldehyde may be oxidised by vanadium(V) through the formation of intermediate free radicals or by the alternative path. We have, therefore, studied the oxidation of benzaldehyde by vanadium(V) in perchloric acid medium. The oxidation of [^{2}H]benzaldehyde was also carried out since it may give information concerning the nature of the rate-determining step. Finally, an attempt was made to compare the present results obtained with those for chromium(VI) oxidation of the same substrate in perchloric acid medium.

Experimental

Reagents.—Inorganic materials were of either B.D.H. AnalaR or Merck G.R. grade. A standard solution of vanadium(V) was prepared by dissolving either ammonium or sodium metavanadate in standard perchloric acid. Perchloric acid solutions were prepared by dilution of 70% $HClO_4$ and were standardised by titration with NaOH to the phenolphthalein end point.

All organic compounds (reagent grade) were further purified by either recrystallisation or redistillation before use. A solution of benzaldehyde in water was made by delivering a known volume of freshly distilled (under an inert atmosphere) benzaldehyde. Acetic acid was heated under reflux for 6 h with excess of potassium dichromate and distilled before use. [^{2}H]Benzaldehyde was prepared[18c] by reduction of benzil (Merck) with lithium aluminium deuteride (Fluka, A.G.) to give the diol followed by the oxidation of diol by lead tetra-acetate, $\nu_{max.}$(film), 2 100 and 2 050 cm^{-1} (lit.,[18c] 4.76 and 4.83 μ); $\delta(CCl_4)$ 7.2—7.9 (m, aromatic H) and no signal for the formyl proton.

Kinetic Measurements.—The experiments were carried out at [vanadium(V)], [PhCHO], [$HClO_4$] 1.0×10^{-2}, 6.0×10^{-2}, and 2.1M, respectively and temperature 323 K unless otherwise mentioned. Solutions of vanadium(V) and the reaction mixture containing organic substrate, perchloric acid, and other reagents (whenever necessary) were separately thermostatted (variation ±0.1 °C). The solutions were then mixed and, at suitable intervals, a portion was withdrawn and quenched in phosphoric acid–sulphuric acid containing a known excess of iron(II) ammonium sulphate. The unchanged iron(II) ion was then titrated against standard dichromate solution using sodium diphenylaminesulphonate as indicator. The reaction was followed to at least 50% consumption of initial oxidant. Generally 8—10 experimental points were taken for each run for the calculation of first-order rate constants (k_{obs}) which were reproducible to within ±3%. Iron(III) was found to have no effect on the organic substrate and vanadium(IV).

Stoicheiometry and Product Analysis.—A mixture of freshly distilled benzaldehyde (2.6 g), sodium metavanadate (3.0 g), perchloric acid (70%, 10 ml), and water (10 ml) was heated under reflux for 4 h under an inert atmosphere. The pale green mixture was cooled and extracted with chloroform (3 × 25 ml). The organic layer was washed with water (10 ml), then extracted with sodium hydrogencarbonate solution (preserved), again washed with water and dried (Na_2SO_4). On removal of the solvent, an oil was obtained (1.5 g) which furnished a 2,4-dinitrophenylhydrazone derivative, m.p. 235 °C, that remained undepressed on admixture with an authentic sample of benzaldehyde 2,4-dinitrophenylhydrazone. This neutral product (1.0 g) was left for aerial oxidation at room temperature for several days until the characteristic smell of benzaldehyde was no longer perceptible. It was treated with excess of dilute sodium hydroxide and the mixture on the usual work-up did not furnish any neutral product. The alkaline solution was acidified (Congo Red) with concentrated hydrochloric acid and the precipitate yielded benzoic acid (1.0 g).

The aforementioned sodium hydrogencarbonate extract was acidified (Congo Red) with concentrated hydrochloric acid and extracted with chloroform (3 × 25 ml). The organic layer furnished crude acid (1.2 g, 80% yield) which was recrystallised from hot water to produce pure benzoic acid (0.9 g). This experiment was repeated several times. When similar experiments were carried out in the absence of vanadium(V) the starting material was recovered to the extent of 95% and benzoic acid was obtained to the extent of only 1—2% showing that perchloric acid was unable to oxidise benzaldehyde under the experimental condition.

Test for Unstable Intermediates.—Waters *et al.*[1] and other workers[18b] have shown that vinyl compounds and mercury(II) chloride can be used as free radical traps. Tests for polymerisation as indicated by gel formation of acrylamide were conducted for a mixture of vanadium(V) and benzaldehyde in the presence of perchloric acid. In contrast to the observation made earlier[18a] in the iridium(IV) oxidation of the same substrate, no visible polymerisation except after long periods was noticed. Mercury(II) chloride also failed to give a visible precipitate during the oxidation of benzaldehyde by this oxidant. It appears that free radicals do not intervene in this reaction. The absence of benzil in the neutral part of the reaction mixture further rules out the possibility that two free radicals dimerise. On the other hand, vanadium(III) is known to form a stable blue-violet compound[19] in concentrated sulphuric acid medium. When the present reaction was carried out in sulphuric acid (*ca.* 9M), initially a deep green solution[19a] was obtained which was concentrated and cooled in ice-cold water for several hours. The resulting solution gave crystals with a blue-violet tinge. This is to be expected if vanadium(III) gives $V(SO_4)_2^-$ in sulphuric acid medium.[19]

Spectrophotometric Evidence for the Intermediate Complex.— Since the complex is unstable, the absorbances of vanadium(V) solutions with and without benzaldehyde were measured at 340 nm [near the absorption maximum of vanadium(V)]. The substrate does not absorb at this wavelength. The concentrations of vanadium(V) and $HClO_4$ were 1.0×10^{-3} and 2.42M, respectively. The absorbances of vanadium(V) solution at 340 nm and in the presence of 0, 1.0×10^{-2}, 3.0×10^{-2}, and 5.0×10^{-2}M-substrate are 0.150, 0.266, 0.322, and 0.524, respectively.

Results

The oxidation of benzaldehyde was studied at different vanadium(V) concentrations in the range $(1.0—8.0) \times 10^{-2}$M at [PhCHO] 1.0×10^{-1}, [$HClO_4$] 2.1M, and temperature 323 K. The average value of the first-order rate constant was $(5.7 \pm 0.15) \times 10^{-5}$ s^{-1} which indicates that k_{obs} is independent of the initial vanadium(V) concentration. The non-linear behaviour of k_{obs} as a function of changing initial concentration of the substrate is suggestive of vanadium(V)–substrate complex formation. Again, the increase in optical density for solutions with benzaldehyde indicates a change of species which in the present reaction is a complex of benzaldehyde and vanadium(V). Plots of $1/k_{obs}$ against 1/[PhCHO] at different temperatures are shown in Figure 1. The rate expression (1) may be suggested

$$-d[V^V]/dt = \frac{kK_e\,[V^V]\,[PhCHO]}{1 + K_e\,[PhCHO]} \qquad (1)$$

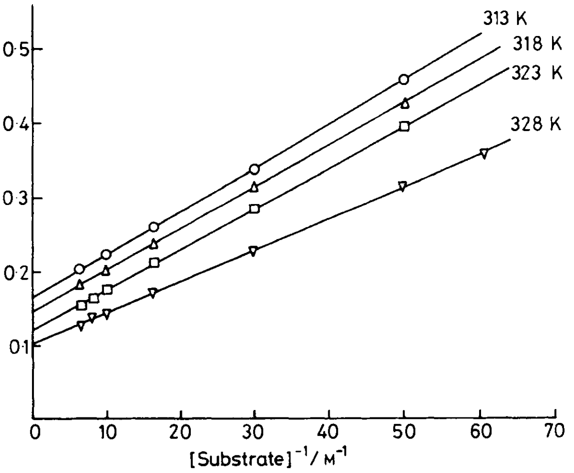


Figure 1. Plots of reciprocal of the first-order rate constants against reciprocal of substrate concentrations at different temperatures: [V^V] 1.0×10^{-2}M, [$HClO_4$] 2.1M

where k and K_e denote the electron-transfer constant and the equilibrium constant for a 1:1 complex. The values of k were calculated from the intercepts of Figure 1 and K_e from the gradients and intercepts of the same figure at different temperatures.

The reaction was studied at different hydrogen ion concentrations varied by the addition of perchloric acid. Two sets of experiments were performed. For the first set of experiments the ionic strength could not be maintained constant at [$HClO_4$] > 4.0M. In another set of experiments when ionic strength was held constant by the addition of sodium perchlorate (I = 4.0M), the reaction was studied at [$HClO_4$] $\leqslant$ 4.0M. The two Hammett correlations, *e.g.* the plots of (i) log k_{obs} against log [$HClO_4$] and (ii) log k_{obs} against $-H_0$, were tested in order to distinguish between cyclic and acyclic mechanisms.[1] The values of Hammett acidity functions were taken from Yates and Wal.[20] The slope of the former plot is unity whereas the same for the latter is significantly less than unity (0.3). The results which are plotted in Figure 2 further confirm that the reaction is first order with respect to [$HClO_4$] irrespective of whether the ionic strength was kept fixed or not. The present observation is, therefore, similar to those reported by earlier workers in the vanadium(V) oxidations of cyclopentanone[4] and cyclobutanols[8] in acidic perchlorate medium. The experimental evidence thus supports the formation of an acyclic complex in the reaction. The effect of changing acetic acid concentration on k_{obs} was examined (Table 1). It has been

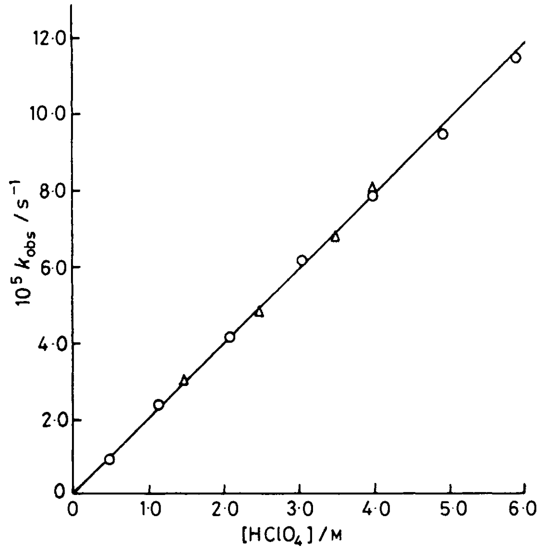


Figure 2. Acidity dependence of the vanadium(V) oxidation of benzaldehyde in aqueous perchloric acid medium. Plot of k_{obs} against [$HClO_4$]: [V^V] 1.0×10^{-2}M, [PhCHO] 6.0×10^{-2}M, T 323 K. △, Constant ionic strength; ○, ionic strength not fixed

Table 1. Effect of solvent composition on first-order rate constant at 323 K. [V^V] 1.0×10^{-2}M, [PhCHO] 6.0×10^{-2}M, [$HClO_4$] 2.1M

% Acetic acid (v/v)	$10^3/\varepsilon$	$10^5\ k_{obs}$/s^{-1}
0	12.82	4.26
20	17.39	5.02
30	19.61	5.99
40	22.40	7.60
50	26.04	8.88

Table 2. Electron transfer constants and equilibrium constants at different temperatures

T/K	K_e/l mol^{-1}	10^5 k/s^{-1}
313	27.5	6.06
318	25.8	6.90
323	24.0	8.33
328	22.6	9.52

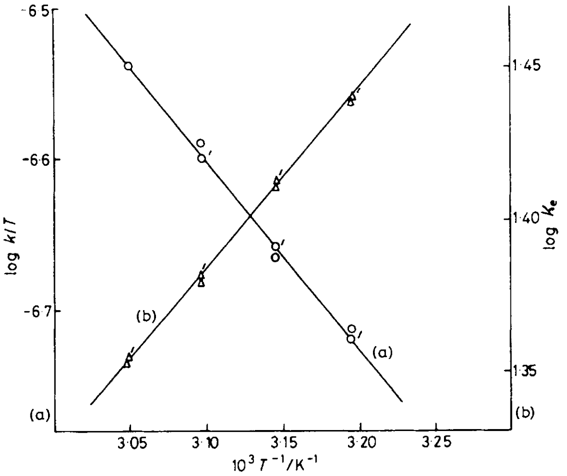


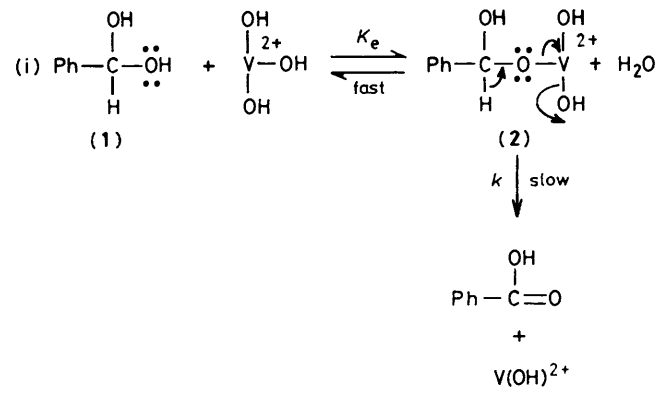
Figure 3. Variation of electron-transfer constants and equilibrium constants with temperature. Plots of (*a*) log k/T against $1/T$ and (b) log K_e against $1/T$: △, ○, experimental points; △′, ○′, least-squares points

reported earlier[10] that upon an increase in the proportion of acetic acid, the dielectric constant of the medium is greatly altered. A plot of log k_{obs} against $1/\varepsilon$ (ε = dielectric constant) is linear with positive slope. This indicates that one of the reactive species is positively charged.[21]

The effect of substituents on the rate of reaction was determined using benzaldehyde and some substituted derivatives in 15% (v/v) acetic acid medium (conditions as in Table 1). The values of 10^5 k_{obs} are 4.5, 19.2, 2.95, and 1.26 s^{-1} in benzaldehyde, *p*-methoxy-, *p*-nitro- and *p*-chlorobenzaldehyde, respectively. Again, the values of K_e for the oxidation of the respective aldehydes are 9.5, 7.2, 10.8, and 11.2 at 328 K. The rate of oxidation usually decreases in the presence of electron-donating groups and increases in the presence of electron-withdrawing groups.[15-17] On the other hand, it has been observed in the present study that the rate of the reaction increases considerably when methoxybenzaldehyde is used and the reverse is the case with nitro- and chloro-benzaldehydes. The results are in agreement with those obtained earlier with hexachloroiridate(IV) oxidations of aromatic aldehydes.[18]

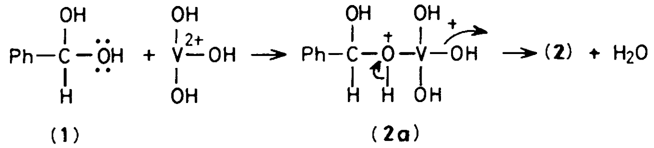
The values of k and K at different temperatures are recorded in Table 2. The values of ΔH^* and ΔH were calculated from the least-square plots (Figure 3) of log k/T against $1/T$ and log K_e *versus* $1/T$, respectively, followed by the calculations of ΔS^* and ΔS for the respective steps. The values of ΔH^* and ΔS^* for the slow step are 23.0 kJ mol^{-1} and -252.8 J K^{-1} mol^{-1} whereas the values of ΔH and ΔS for the equilibrium step are -11.6 kJ mol^{-1} and -9.45 J K^{-1} mol^{-1}, respectively.

[^{2}H]Benzaldehyde was oxidised under the same conditions as for the oxidation of ordinary benzaldehyde. The values of k_{obs} are 5.70×10^{-5} and 1.18×10^{-5} s^{-1}. The isotope effect, k_H/k_D, is 4.8 compared with the value of 4.3 found in the chromic acid oxidation of benzaldehyde in perchloric acid medium. The result indicates that the carbon–hydrogen bond is cleaved in the rate-determining step.



$$\text{(ii) } V(OH)^{2+} + V(OH)_3^{2+} \xrightarrow{\text{fast}} 2\ V(OH)_2^{2+}$$

Scheme 1.



Scheme 2.

Discussion

The principal observations concerning the oxidation of benzaldehyde by vanadium(V) may be summarised as follows. The rate of the reaction is found to be proportional to the first power of oxidant and hydrogen ion concentrations. The results indicate that benzaldehyde reacts with the oxidant to give products through the formation of an intermediate complex. It has been confirmed that benzaldehyde and not benzil was present in the neutral part of the reaction mixture. This excludes the possibility of the formation of $\mathrm{Ph\dot{C}{=}O}$ during the reaction. Moreover, two moles of sodium vanadate oxidised one mole of benzaldehyde to benzoic acid.

Though vanadium(V) is amphoteric, oxidation by it in acidic solution (>0.005M) involves cationic species.[22,23] In the acidity region (pH $\leqslant$ 1.0) vanadium(V) exists as the bright yellow pervanadyl ion VO_2^+ which is also believed to exist in hydrated form $[VO_2{\cdot}2H_2O]^+$ or $[V(OH)_4]^+$. It has been established[1] that the protonated form of the oxidant is more reactive in acid medium. In perchloric acid medium, protonated species such as $VO(OH)^{2+}$ and VO^{3+} or their hydrates $V(OH)_3^{2+}$ and $V(OH)_2^{3+}$ are formed. The slope of a plot of log k_{obs} against log $[HClO_4]$ is unity. The first-order dependence on $[H^+]$ may be explained by different mechanisms. Initial protonation of unhydrated aldehyde may occur to give $\mathrm{Ph\overset{+}{C}HOH}$ or a proton may be added to one of the hydroxy groups of the hydrated aldehyde[13] to give $PhCHOH(OH_2^+)$. When a reaction takes place between ions of similar charge, the rate decreases with a decrease in the dielectric constant of the medium. The results (Table 1) rule out the possibility of the reaction taking place between two similarly charged molecules. On the other hand, it is possible that $V(OH)_3^{2+}$ which is formed by the reaction of H^+ and $V(OH)_4^+$ reacts with benzaldehyde and/or hydrated benzaldehyde to give an intermediate complex prior to electron transfer. The hydrates of aliphatic and aromatic aldehydes are well known[14,15] and the majority of the reactions have been shown to occur through hydrated aldehydes. It is suggested that hydrated aldehyde reacts with the reactive vanadium(v) species to give a 1:1 intermediate complex followed by the decomposition of the complex to give products as shown in Scheme 1.

The formation of the intermediate complex (**2**) by the condensation of the two reactive species seems unlikely and during the transformation of (**1**) to (**2**) the transition state (**2a**) is probably formed which rapidly becomes (**2**) under the experimental condition (Scheme 2).

It has been shown[15a] in the chromic acid oxidation of aromatic aldehydes that H^+ is initially added to $HCrO_4^-$ to give H_2CrO_4 which then reacts with hydrated aldehyde to give products through the formation of an intermediate ester. Since vanadium(v) in its highest oxidation state (+5) has close similarities with its successor in the first transition series, *i.e.* chromium in its highest oxidation state (+6) and the standard redox potential[24] of the $HCrO_4^-$–Cr^{3+} and V^{5+}–V^{4+} couples is 1.195 and 1.00 V, respectively, the possibility that the present reaction occurs through intermediate complex formation does exist. The present observation is reminiscent of the effect noted by earlier workers[15a] in the chromic acid oxidation of aromatic aldehydes in perchloric acid medium. It appears that vanadium(v) behaves as a two-electron transfer oxidant although the one-electron reduction of vanadium(v) cannot be totally ruled out. The lower activation enthalpy of 23.0 kJ mol^{-1} obtained in this study, compared with the much higher values found in the reactions where vanadium(v) behaves as a one-electron[25,26] transfer oxidant, corroborates the suggested mechanism.

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